1,086,753

PATENT SPECIFICATION

NO DRAWINGS

1,086,753

Date of Application and filing Complete Specification: Feb. 3, 1965.

No. 4700/65.

Application made in United States of America (No. 343,130) on Feb. 6, 1964.

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COMPLETE SPECIFICATION

Development of Electrostatic Images with Liquid Developer

ERRATUM

SPECIFICATION No. 1,086,753

Page 1, line 1, *for* "DENNISON MANUFACTURING LIMITED" *read* "DENNISON MANUFACTURING CO. LIMITED"

THE PATENT OFFICE
13th November 1967

comprising coloured toner particles suspended in an insulating liquid. It is known that the insulating liquid should have high volume resistivity, preferably at least 10^9 ohm-centimetres and low dielectric constant, preferably 3.4 or less. Suitable liquids include aromatic hydrocarbons such as benzene, toluene and xylene; aliphatic hydrocarbon such as hexane, cyclohexane and heptane; halogenated hydrocarbons; silicone oils; and mixtures thereof. The suspended toner particles, usually finely-divided pigments or pigmented resins, are electrostatically charged and develop the latent image by migration to the image surface under influence of the image charge. The resulting prints are usually fixed by fusing the toner particles either directly to the image surface or to another surface following transfer of the toner particles thereto.

To obtain a positive print by development as described above, the suspended toner

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tertiary and quaternary amines.

While both materials (1) and (2) must be present and should be in solution at the temperature used for image development the amounts thereof are not critical if used in effective quantities which do not seriously lower the dielectric properties of the resulting solution in the insulating liquid; that is, provided amounts are used which do not lower the volume of resistivity of the insulating liquid-additive solution below 10^9 ohm-centimetres or raise the dielectric constant above 3.4. Small quantities are beneficial in enhancing the contrast of the print and/or the stability of the developer suspension. Increasing amounts typically improve the developer until a maximum is reached. Beyond such maximum, increasing amounts have little effect until the insulating qualities of the suspending medium are adversely affected. Preferably, from 0.01 to 5% of the metal salt (1) and from 0.01 to 6%

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COMPLETE SPECIFICATION

Development of Electrostatic Images with Liquid Developer

We, DENNISON MANUFACTURING LIMITED, a Company registered under the Laws of Great Britain, of Colonial Way, Watford, Hertfordshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to electrophotography, and more particularly to improvements in the development of visible images from latent electrostatic images by the use of liquid developers.

In electrophotography, latent electrostatic images are formed on a photoconductive surface of a recording element by uniformly charging the surface thereon, as by a corona discharge device in the dark, followed by exposure to light in the desired image pattern. Such images have been heretofore developed or rendered visible by use of liquid developers comprising coloured toner particles suspended in an insulating liquid. It is known that the insulating liquid should have high volume resistivity, preferably at least 10^9 ohm-centimetres and low dielectric constant, preferably 3.4 or less. Suitable liquids include aromatic hydrocarbons such as benzene, toluene and xylene; aliphatic hydrocarbon such as hexane, cyclohexane and heptane; halogenated hydrocarbons; silicone oils; and mixtures thereof. The suspended toner particles, usually finely-divided pigments or pigmented resins, are electrostatically charged and develop the latent image by migration to the image surface under influence of the image charge. The resulting prints are usually fixed by fusing the toner particles either directly to the image surface or to another surface following transfer of the toner particles thereto.

To obtain a positive print by development as described above, the suspended toner particle should carry an electrostatic charge opposite to the charge present in the electrostatic latent image. Latent images currently used are negatively charged and the toner particles should carry a positive charge to obtain a positive print therefrom. The present invention provides liquid toner compositions having positively charged particles.

According to the present invention, a liquid toner composition, for developing an electrostatic image, comprises finely divided toner particles suspended in an insulating liquid having dissolved therein, a mixture of (1) a metal salt of an organic acid, wherein the metal has a valency of 3 to 4, and (2) an amine, the salt and the amine being chemically non-reactive in the developer, the insulating liquid solution of (1) and (2) having a volume resistivity of at least 10^9 ohm-centimetres and a dielectric constant not greater than 3.4. The term amine, is intended to include ammonia and primary, secondary, tertiary and quaternary amines.

While both materials (1) and (2) must be present and should be in solution at the temperature used for image development the amounts thereof are not critical if used in effective quantities which do not seriously lower the dielectric properties of the resulting solution in the insulating liquid; that is, provided amounts are used which do not lower the volume of resistivity of the insulating liquid-additive solution below 10^9 ohm-centimetres or raise the dielectric constant above 3.4. Small quantities are beneficial in enhancing the contrast of the print and/or the stability of the developer suspension. Increasing amounts typically improve the developer until a maximum is reached. Beyond such maximum, increasing amounts have little effect until the insulating qualities of the suspending medium are adversely affected. Preferably, from 0.01 to 5% of the metal salt (1) and from 0.01 to 6%

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of the amine (2) is used, with a total of between 1 and 6.01% of (1) and (2) together being present in the developer, all percentages being based on the total weight of toner particles present therein. Most preferably, the two additives are used in substantially equal weight quantities.

Examples of suitable metal salts (1) are the trivalent and tetravalent cation salts of aluminium, iron, thorium, zirconium, lanthanum, germanium, tin, vanadium or thallium and any organic acid, whether mono or poly basic, for example, octoic, stearic, rosin, polymerized rosin, naphthenoic, N-tallow β-imino dipropionic, and succinic acids. The salts should be substantially soluble in the insulating liquid and be chemically non-reactive in the developer, and, for stability, are preferably of low volatility.

As the second additive (2), any organic amine, including ammonia, can be used provided it is substantially soluble and chemically non-reactive in the developer. In addition to ammonia, examples include tetraethyl ammonium chloride; Amine C of the Geigy Chemical Company, a substituted imidazoline alicyclic amine; N-coco-morpholine, the Armeens and Duomeens of Armour and Company (Armeen and Duomeen are Registered Trade Marks), for example Armeen DMSD, a tertiary dimethyl soya amine. Duomeen TDO, a tallow amine dioleate, and Duomeen 12, n-lauryl propylene diamine; the polyethyoxylated aliphatic amines available from Armour and Company as Ethomeens and Ethoduomeens (Ethomeen and Ethoduomeen are Registered Trade Marks) and preferably the organic acid esters thereof; and polymeric amines such as Lube Oil 564 of Du Pont, a copolymer of laurylmethacrylate and diethylaminoethylmethacrylate, and similar materials such as those described as oil additives in United States of America Patents Specification Nos. 2,737,452 and 3,008,813, especially those described in the third column of the latter patent as a second class of polymeric additives, and defined as nitrogen-containing addition-type copolymers of an amine-free monomer containing one ethylene linkage and an aliphatic hydrocarbon chain of from 8 to 18 carbon atoms with a monomer containing an amino group and one polymerizable ethylene linkage. While low molecular weight organic nitrogen compounds are operative in providing enhanced toner charge and print contrast, higher molecular weight materials, preferably polymeric, are preferred for their low volatility and protective colloid function which aids in providing stability in the suspension during storage and use. Tertiary and quaternary amines of high molecular weight are most preferred.

While the additives (1) and (2) are chemically non-reactive in the developer as stated above, no primary bonds of the covalent, polar, ionic or metallic type being formed in the developer, some secondary association between the additives themselves is believed to occur. For example, mixtures of both additives in Odourless mineral spirits generally have higher conductivities than either alone in like quantities. While the type of association is not understood, it is believed to involve the amine nitrogen atom or atoms and the carboxyl groups of the salt. For example, infrared spectra of solutions of equal weight quantities of both additives in Odourless mineral spirits, aged at least 48 hours, show a measurable decrease in the absorbance at 6.3 microns, a peak attributed to the carboxyl group of the salt (1), over the spectra of a like solution of the salt alone.

The following examples are for the purpose of illustration, Example 2 (c) being currently preferred. All parts are by weight unless otherwise stated.

The toner particles indicated in Examples 1—7 were prepared as follows:—

Toner Particles

Nigrosine SSB dye	40
Santicizer 9 (Santicizer is a Registered Trade Mark)	30
Santowax M	20
Age Rite Resin D	10

The last three ingredients were melted together, the dye dissolved therein and the melt solidified by cooling and then ground. Nigrosine SSB is a black dye obtained from the National Aniline Company, Santowax M and Santicizer 9 are respectively a meta terphenyl and a mixture of ortho and para toluene sulphonamides obtained from the Monsanto Chemical Company, and Age Rite Resin D is a polyquinoline obtained from the R. T. Vanderbilt Company. Many other suitable toner compositions are known and can also be used.

EXAMPLE 1

Developer Concentrates

Material	a	b	c	d	e
Toner particles	10	10	10	10	10
Odourless mineral spirits (OMS)	39	39	39	39	39
Aluminium tristearate	.01	.05	0.1	0.3	0.5
Lube Oil	.59	.55	0.5	0.3	0.1

The foregoing concentrates were prepared by dissolving the aluminium salt and the Lube Oil 564 in the OMS, adding the toner particles, and ballmilling the mixture in a porcelain mill with steel balls for sixteen hours. OMS is a mixture of paraffin hydrocarbons obtained from the American Mineral Spirits Company having a distillation range from 352° to 390° F. and a flashpoint of 125° C.

One-fourth part of each of the above compositions was further diluted with 100 parts of additional OMS. A conventional electrofax recording element comprising paper coated with photo-conductive zinc oxide suspended in a resinous binder was processed to provide a latent image by exposure to a corona discharge device at a 6KV negative potential and discharged with light in an image pattern. Recording elements were then developed by immersion in each of the foregoing diluted compositions and fixed by heating for a few seconds above the melting temperature of the toner particles, for example 125° C. Prints with good contrast and good definition were obtained. Composition *d* having the metal salt and organic esters present in equal weight amounts provided the best prints and the best stability of liquid toner against settling.

EXAMPLE 2

Additional compositions involving the ingredients of Example 1 were made as follows, the dispersant mixture being equal weight amounts of the aluminium salt and Lube oil 564 stated above.

Material	a	b	c	d	e
Toner particles	10	10	10	10	10
Dispersant mixture	0.3	0.5	1.0	5.0	7.5
OMS	39.5	39.1	38.5	34.5	30.32

Again the dispersant mixture was first dissolved in the OMS, the toner particles added, and the mixture ballmilled for sixteen hours. One-fourth part of each composition was further diluted with 100 parts additional OMS and prints developed as above-described in Example 1. Good contrast and definition were obtained.

EXAMPLE 3.

Toner particles	10
Aluminium tristearate	0.5
Nitrogen Compound	0.5
OMS	38.25

The resulting mixture was ballmilled for sixteen hours to provide a fluid dispersion, and one-fourth part thereof further diluted with 100 parts additional OMS. Electrostatic prints as previously described were prepared and provided excellent contrast. The nitrogen compound used above was prepared by esterifying three moles of oleic acid with one mole of Ethomeen C/15, followed by neutralization of the resulting amine salt with caustic. Ethomeen C/15 is the reaction product of five moles ethylene oxide with one mole coco amine. Ethomeen C/15 is useful without esterification but the ester is preferable, apparently due to a reduced tendency to lower the insulating properties of its solution with OMS.

EXAMPLE 4

The same as Example 3 above, except that the ester was a terpolymer of 40 parts laurylmethacrylate, 10 parts diethylaminoethylmethacrylate and 40 parts stryrene.

EXAMPLE 5.

The same as Example 4 above, excepting that the thorium salt of rosin acid was substituted for the aluminium tristearate. Prints with good contrast were obtained by following the procedure described in Example 1.

EXAMPLE 6

The same as Example 5 above, excepting that ferric stearate was used instead of the thorium salt.

EXAMPLE 7

The same as Example 5 above, excepting that the zirconium salt of rosin acid was used in place of the thorium salt.

EXAMPLE 8

Toner Particles

Carbon Black	10
Rosin	90

The finely divided carbon black was suspended in the melted rosin, the mixture cooled and ground. A developer concentrate was prepared therefrom as follows:

Concentrate

Toner particles	10
Dispersant mixture of Example 2	1.0
OMS	38.25

One-fourth parts of the above concentrate were diluted with an additional 100 parts OMS and prints prepared therefrom as described in Example 1. Prints with excellent contrast and definition were obtained.

EXAMPLE 9

Nigrosine SSB	600
Santicizer 9	400

Toner particles were prepared by dissolving the dye in the melted Santicizer 9, cooling, and grinding.

Toner concentrate

Toner particles, above	10
OMS	37
Aluminium Dresinate 731	0.35
Nitrogen compound, one of:	
(1) Duomeen TDO	1
(2) Armeen DMSD	1
(3) N-coco-morpholine	1
(4) Duomeen 12	1
(5) Amine C	1
(6) Tetraethyl Ammonium chloride	0.1
(7) Anhydrous ammonium	

The resulting mixtures were ball-milled for sixteen hours to provide fluid dispersions and one-fourth part of each further diluted with 100 parts additional OMS. Electrostatic prints prepared as previously described provided excellent contrast. The anhydrous ammonia example was prepared by bubbling the gas through the OMS for about 25 minutes.

Aluminium Dresinate 731 was prepared by aqueous cation exchange between a soluble aluminium salt and Dresinate 371, the sodium salt of rosin acids obtained from Hercules Powder Company.

In all of the foregoing Examples omission of either of the additives results in a less stable suspension which provides a print with faint contrast. For reasons not thoroughly understood, the two additives, together, materially improve contrast, believed to be due to increasing the electrostatic charge on the suspended toner particles. By proper choice of additive, substantially improved suspension and dispersion properties are simultaneously obtained.

WHAT WE CLAIM IS:—

1. A liquid toner composition, for developing a latent electrostatic image, comprising finely divided toner particles suspended in an insulating liquid having dissolved therein a mixture of (1) a metal salt of an organic acid, wherein the metal has a valency of 3 to 4, and (2) an amine, the salt and the amine being chemically non-reactive in the developer, the insulating liquid solution of (1) and (2) having a volume resistivity of at least 10^9 ohm-centimetres and a dielectric constant not greater than 3.4.

2. A toner composition as claimed in Claim 1 having dissolved therein between 0.01 and 5% of the metal salt (1) and between 0.01 and 6% of the amine (2), between 1 and 6.01% of salt and amine together being present, the percentages being based on the weight of toner particles present in the composition.

3. A toner composition as claimed in Claim 2 wherein salt and amine are present in equal weight amounts.

4. A toner composition as claimed in Claim 1 or Claim 2 or Claim 3 wherein the amine is a addition-type copolymer of an amine-free monomer containing one ethylene linkage and an aliphatic hydrocarbon chain of from 8 to 18 carbon atoms with a monomer containing an amino group and one polymerizable ethylene linkage.

5. A toner composition as claimed in Claim 4 wherein the metal salt is a trivalent or tetravalent salt of either aluminium, iron, thorium, zirconium, lanthanum, germanium, tin, vanadium, or thallium, with either octoic, stearic, rosin, polymerized rosin, naphthenoic, N-tallow β-imino dipropionic, or succinic acid.

6. A toner composition as claimed in Claim 2 or Claim 3 wherein the metal salt is aluminium tristearate and the nitrogen compound is polylaurylmethacrylate-diethylaminoethylmethacrylate.

7. A toner composition as claimed in Claim 2 or Claim 3 wherein the metal salt is aluminium tristearate and the nitrogen compound is a terpolymer of octadecencylmethacrylate, diethylaminoethylmethacrylate and styrene.

8. A toner composition as claimed in Claim 2 or Claim 3 in which the metal salt (1) is aluminium tristearate and the compound (2) is an ester of an ethoxylated aliphatic amine.

9. A toner composition as claimed in Claim 2 or Claim 3 wherein the salt is the thorium salt of rosin acid and the nitrogen compound is a terpolymer of laurylmethacrylate, diethylaminoethylmethacrylate and styrene.

10. A toner composition as claimed in Claim 2 or Claim 3 wherein the salt is ferric stearate and the nitrogen compound is a terpolymer of laurylmethacrylate, diethylaminoethylmethacrylate and styrene.

11. A toner composition as any one of those described in any of the foregoing examples.

12. A method of developing a latent electrostatic image comprising the step of contacting the image with a toner composition as claimed in any of the preceding claims.

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